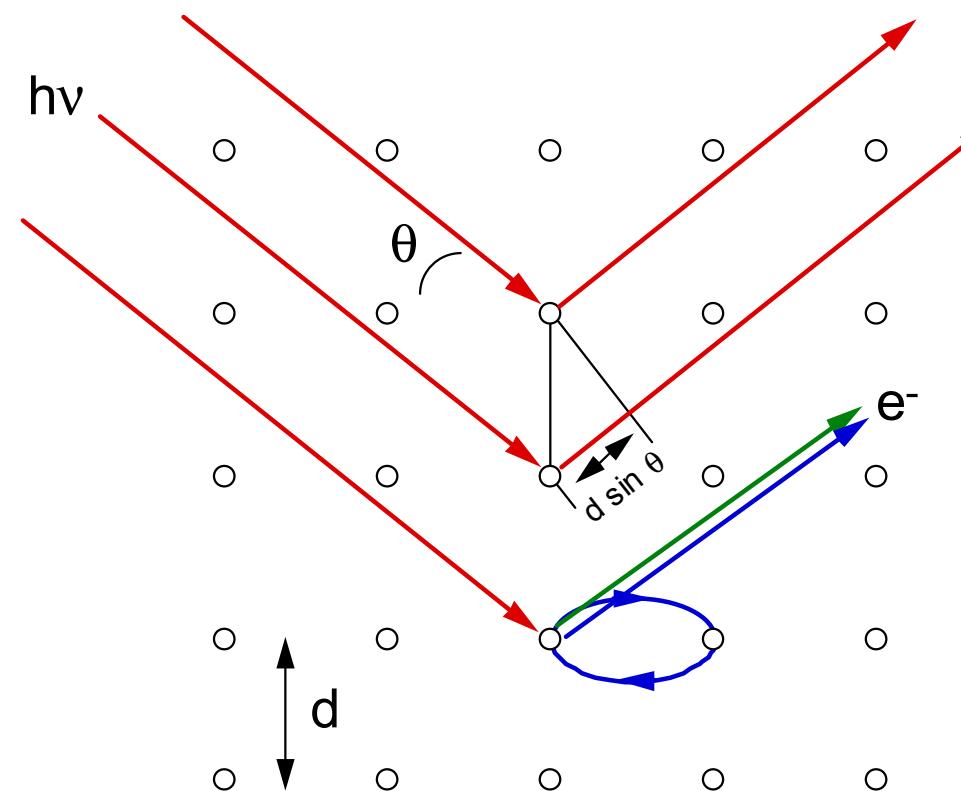


NIST: XAFS, Diffraction, XPS, and Industry

- Patrick Lysaght (**SEMA TECH**)
 - *HfO₂ gate stacks*
- Hao Li (**Motorola**)
 - *SrTiO₃ ferroelectric memory*
- Matthew Erdtmann (**AmberWave**)
 - *Strained Si*

- *Why EXAFS and other techniques?*
 - EXAFS is *model dependent*.....
- *Why EXAFS and X-ray Diffraction?*
 - EXAFS most sensitive to *SRO*
 - Diffraction most sensitive to *LRO*

EXAFS and Diffraction



$$n\lambda = 2d \sin(\theta) \text{ (Bragg's Law)}$$

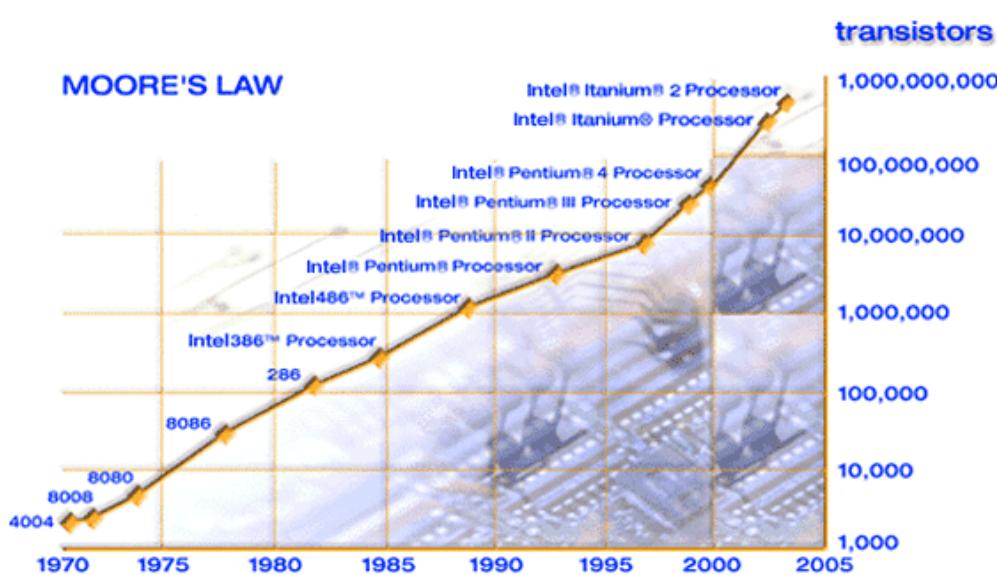
$$\chi(k) = N f(k) \sin(2kr + \phi(k)) \text{ (Stern's Law)}$$

- *Diffraction Anomalous Fine Structure, Valence X-ray Standing Waves, Glancing Incidence XAFS, etc.,*
- *Diffractometer makes a great XAFS sample holder!*

Why are films thin?

- *Material, time, toxicity, and expense.*
- *Moore's Law.*
- *Critical Thickness.*

Nanoelectronics

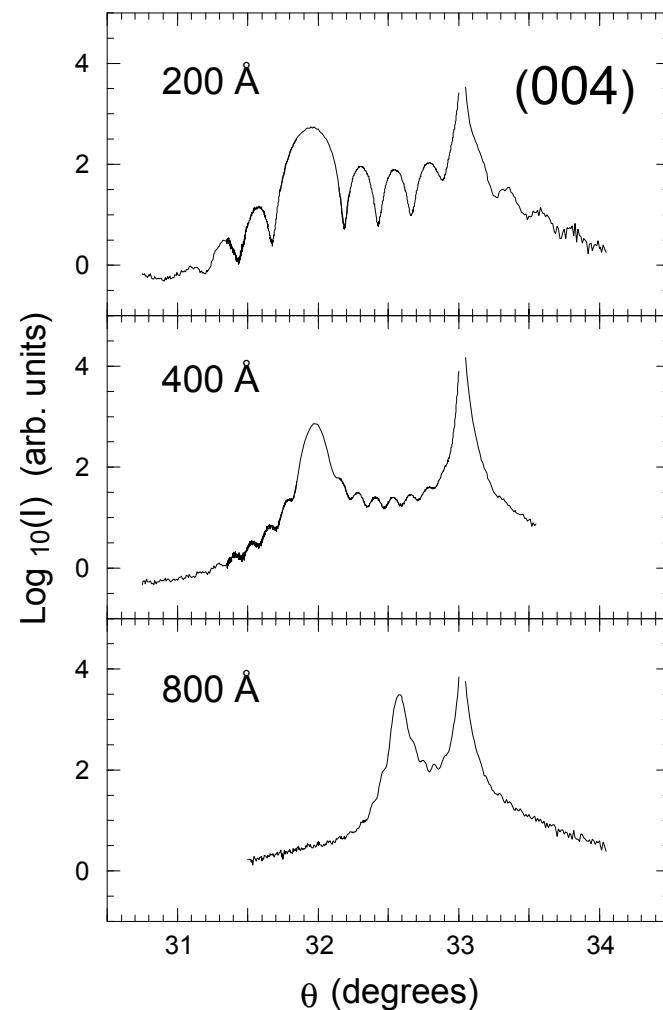


Other Moore technologies

- Minimum feature size of ICs
- Magnetic storage media
- Digital photography pixel density
- CPU speed...

- Similar Moore's trend is seen in the minimum feature size.
- Gate oxide barriers are below 10nm. 1 nm in some cases.
- How does one study materials properties at these length scales?
- How does synchrotron radiation tools help address these needs?
 - Phase ID
 - Atomic fraction measurements
 - Bond lengths
 - Coordination
 - Phase stability
 - Cation site distribution and valency

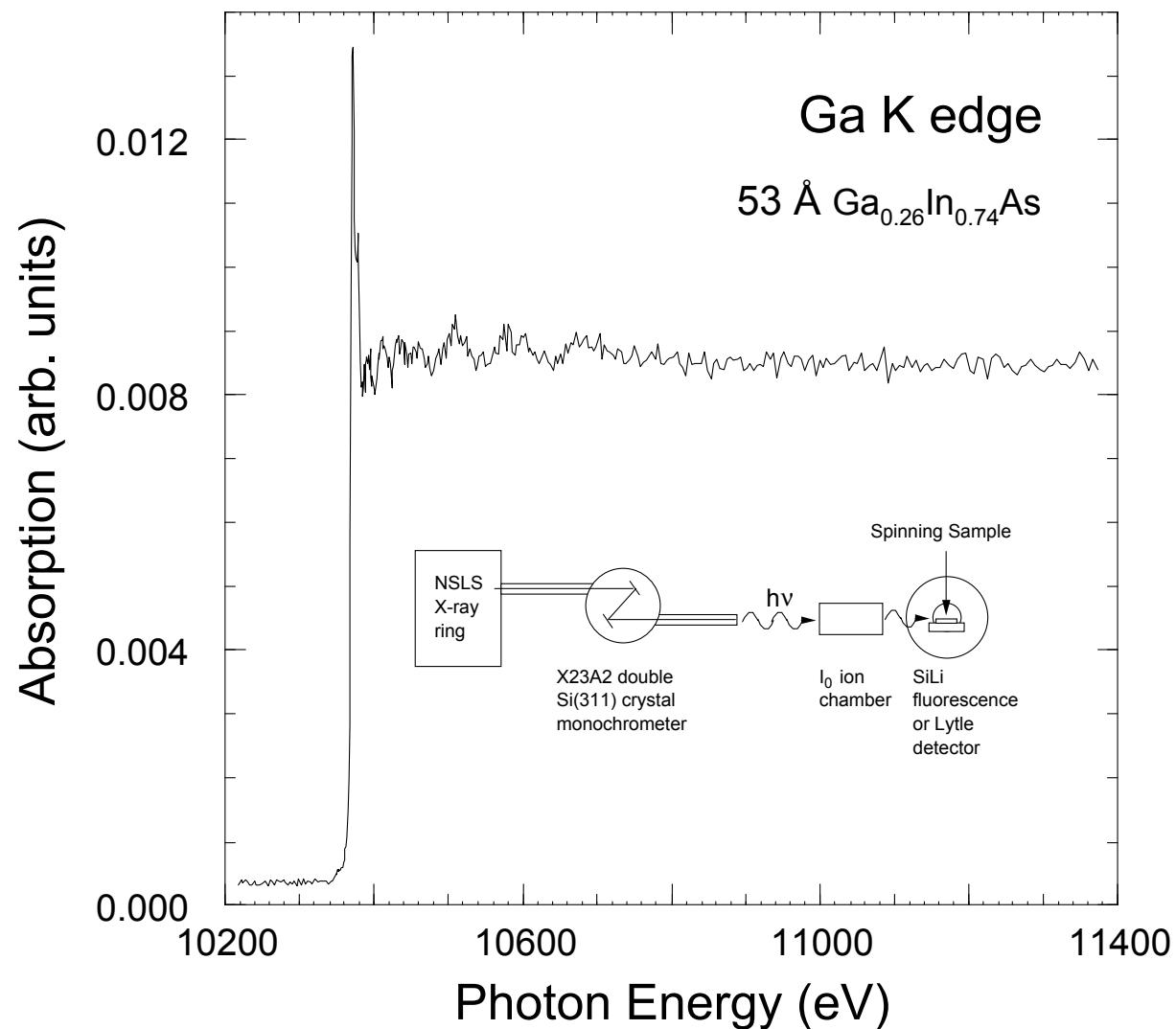
XRD $\text{Ga}_{0.78}\text{In}_{0.22}\text{As}$ on $\text{GaAs}(001)$



Why work with industry?

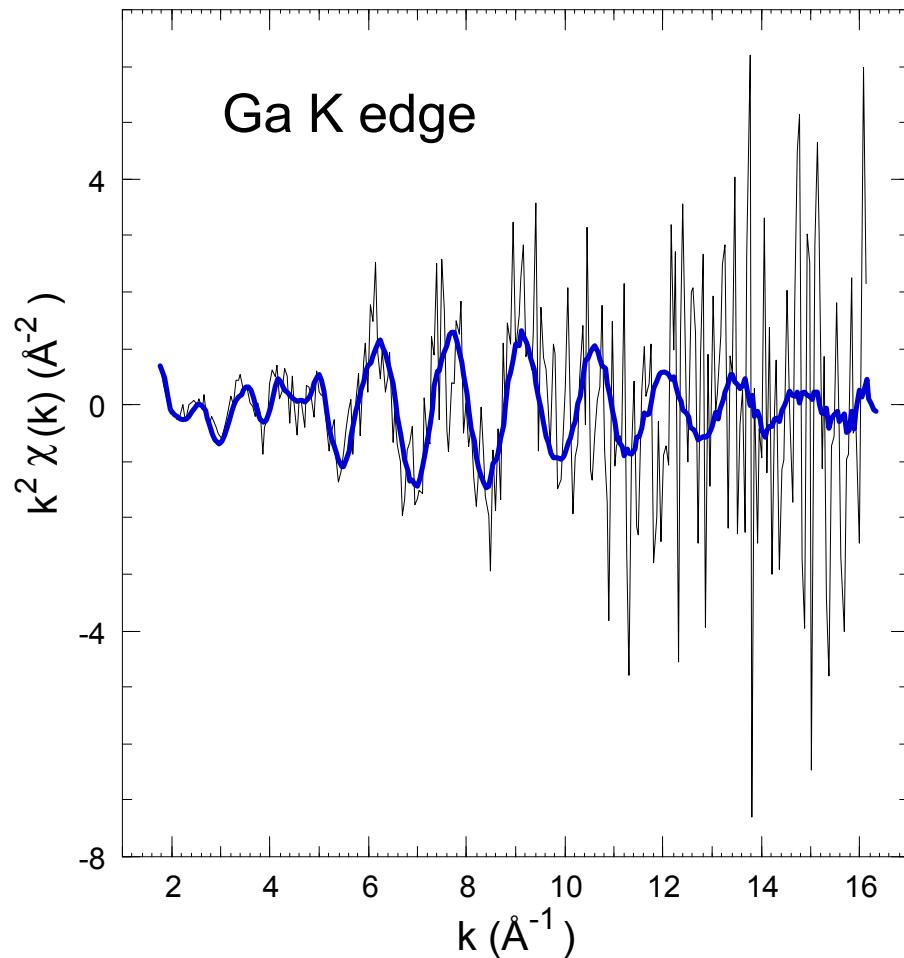
- *Interesting.*
- *NIST = Commerce!*
- *Great Samples.*
- *Great Characterization, but not Synchrotron!*

XAFS Experimental Setup for thin films

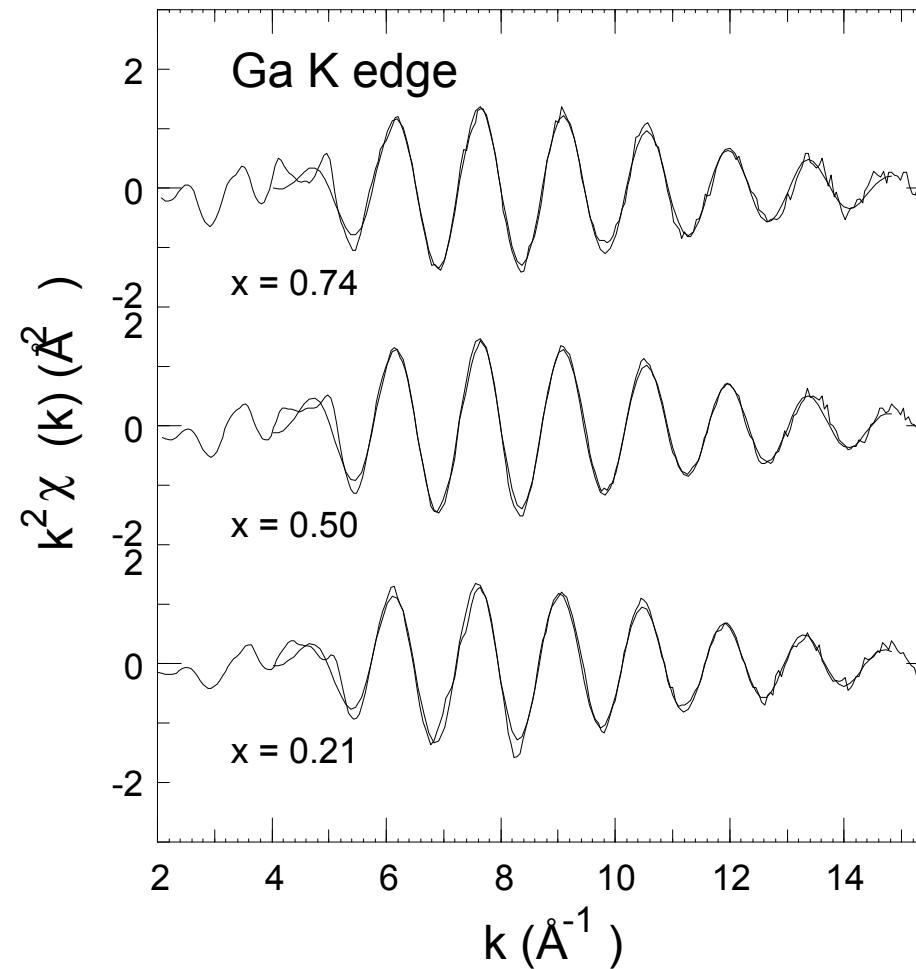


EXAFS Beamline Requirements

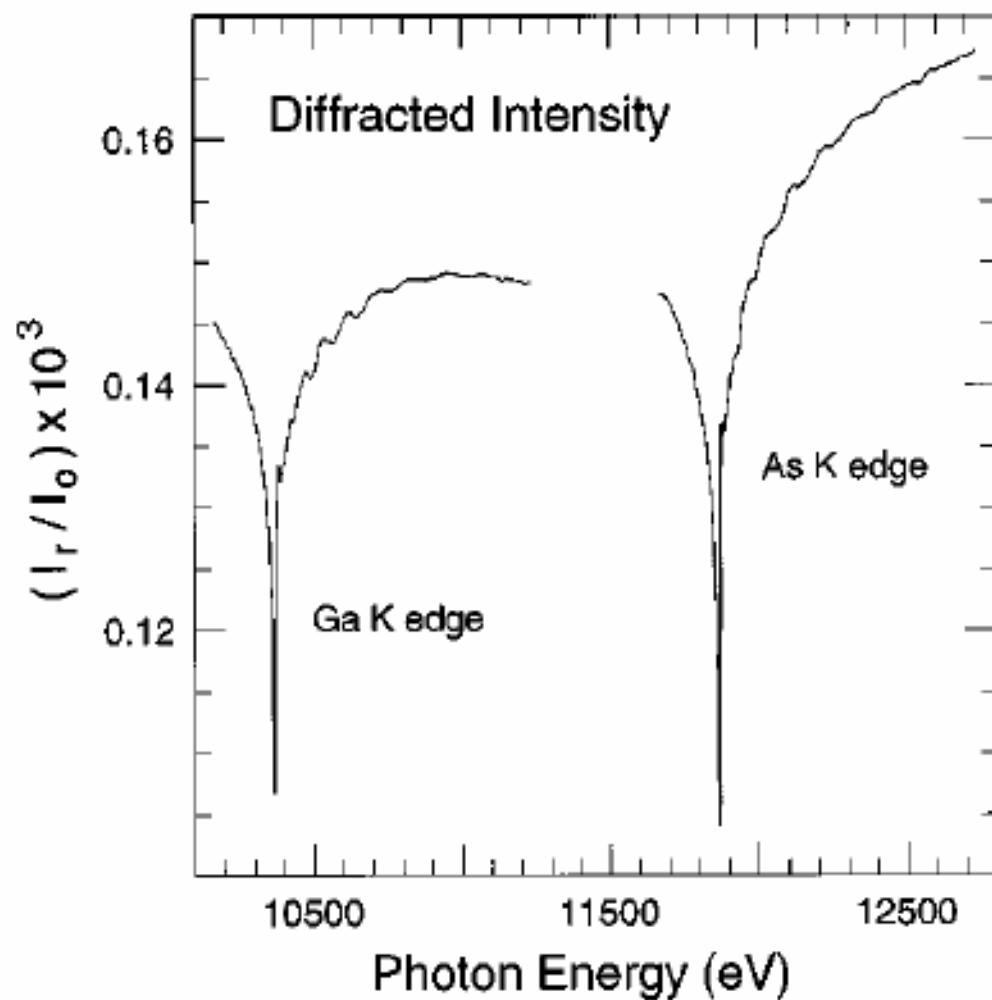
- *Stability*
- *Reproducibility*
- *Scannability*
- *Focusing*
- *High Flux*
- *High Resolution*
- *High S/B detectors*
- *Espresso*
 - *Experiment vs. Measurement*



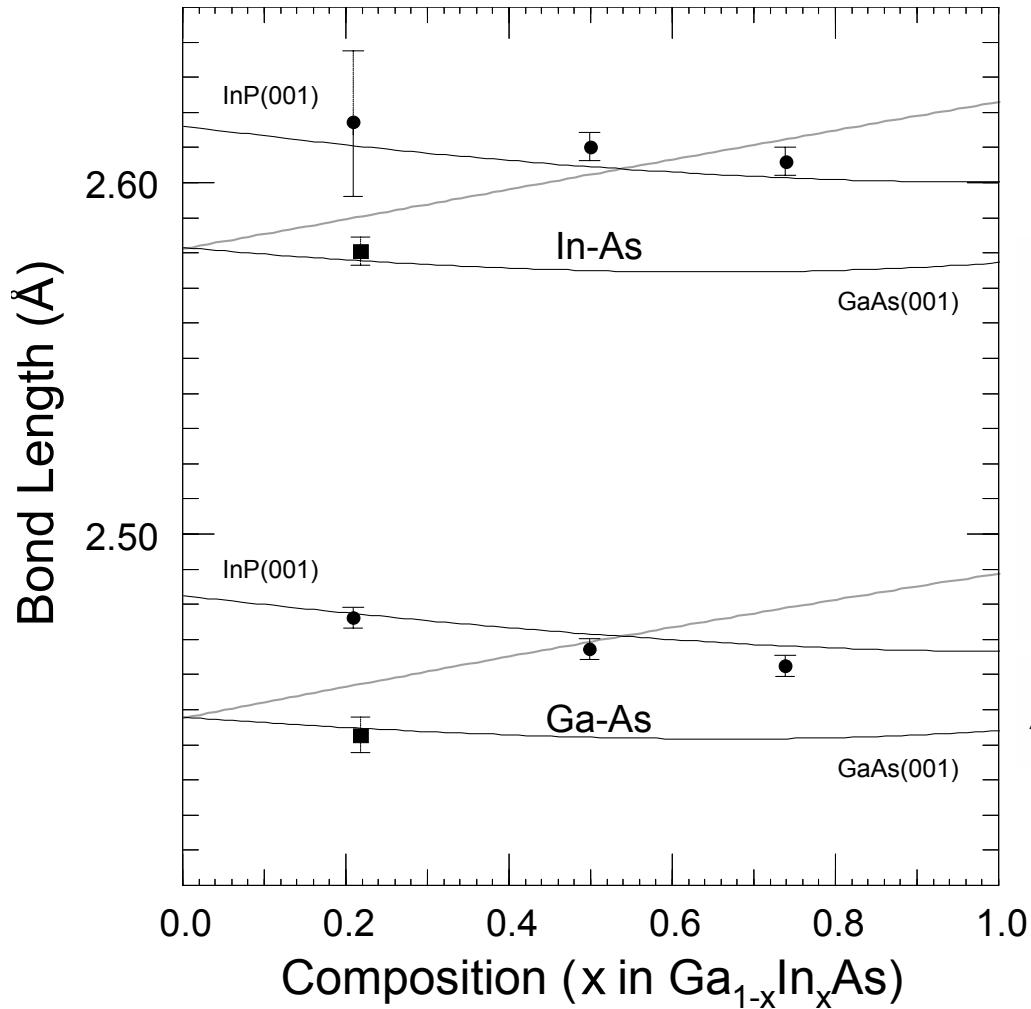
“Raw” Data and Fits



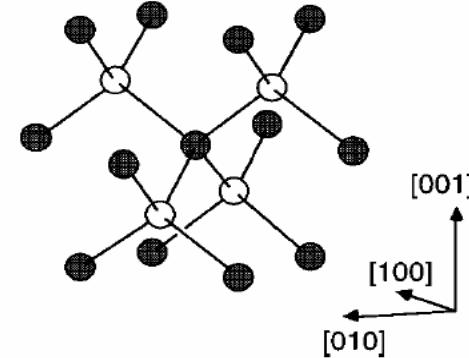
Diffraction Anomalous Fine Structure (DAFS)



Theory and Experiment! ($1\% \text{ strain} \approx 1 \text{ GPa}$)



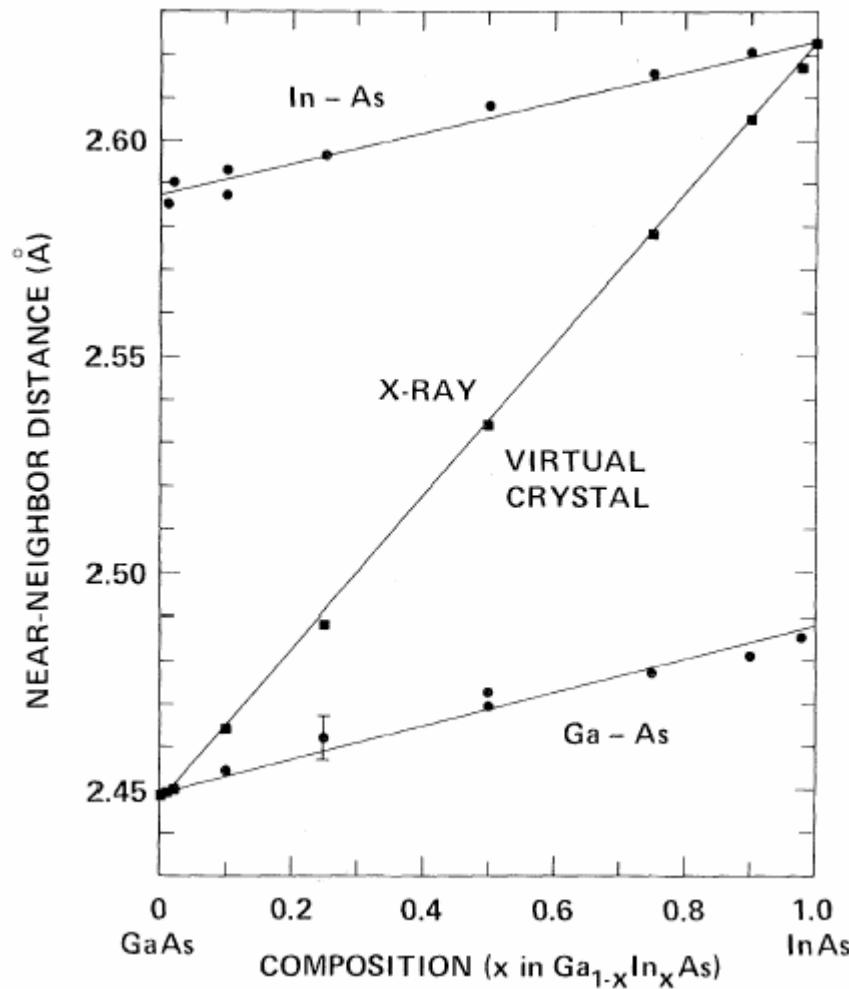
16 Bond Random Cluster Calculation



$$\Delta E = \sum_s \frac{\frac{3}{8} \alpha_s (\mathbf{r}_s^2 - r_{s,0}^2)^2}{r_{s,0}^2} + \sum_{s < t} \sum_t \frac{\frac{3}{8} \beta_{s,t} (\mathbf{r}_s \cdot \mathbf{r}_t - \mathbf{r}_{s,0} \cdot \mathbf{r}_{t,0})^2}{r_{s,0} r_{t,0}}$$

$$x_j^0 = g_j x^j (1-x)^{4-j}$$

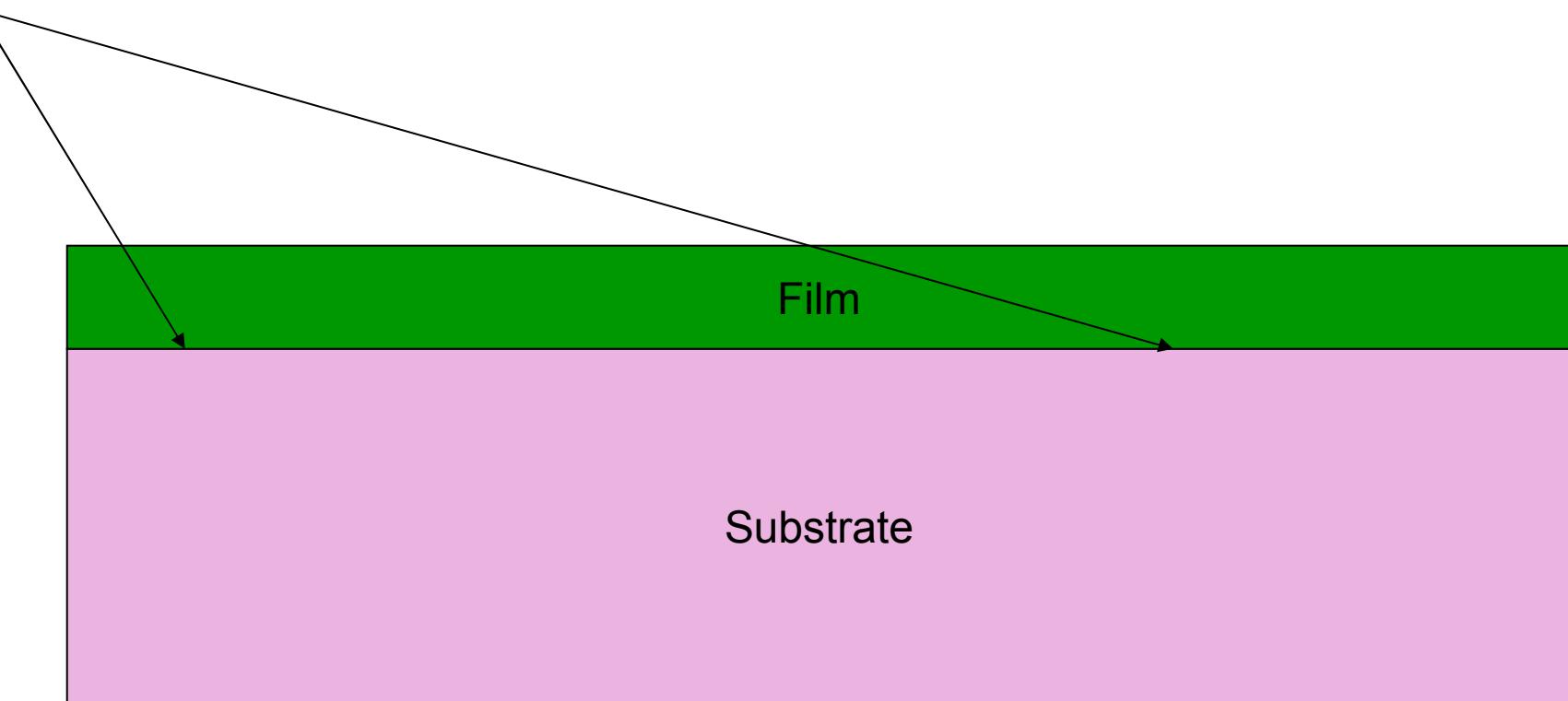
*J.C. Mikkelsen, Jr. and J.B. Boyce, Atomic-Scale Structure of Random Solid Solutions: Extended X-ray-Absorption Fine-Structure Study of $\text{Ga}_{1-x}\text{In}_x\text{As}$, Phys. Rev. Lett. **49**, 1412 (1982).*



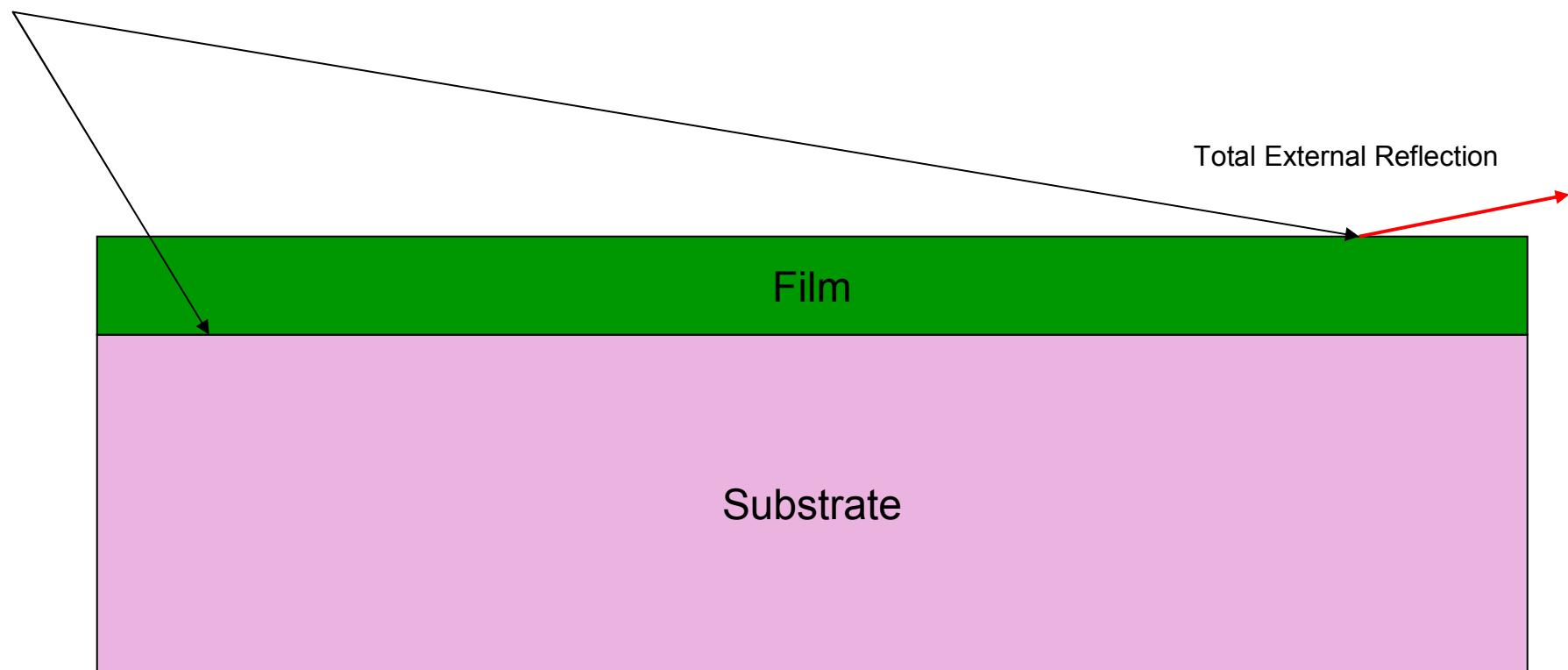
Glancing Incidence XAFS



X rays



X rays



Film

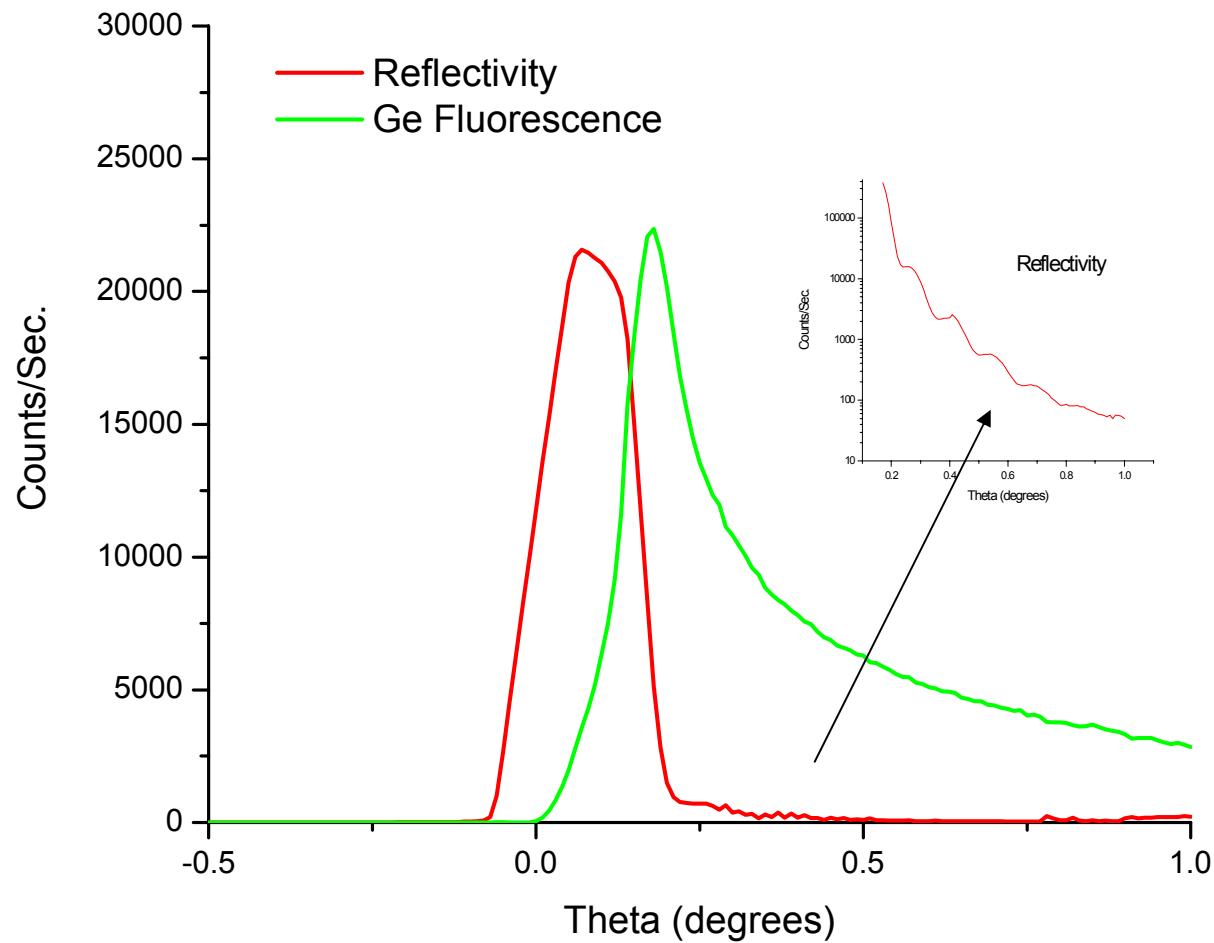
Substrate

Total External Reflection

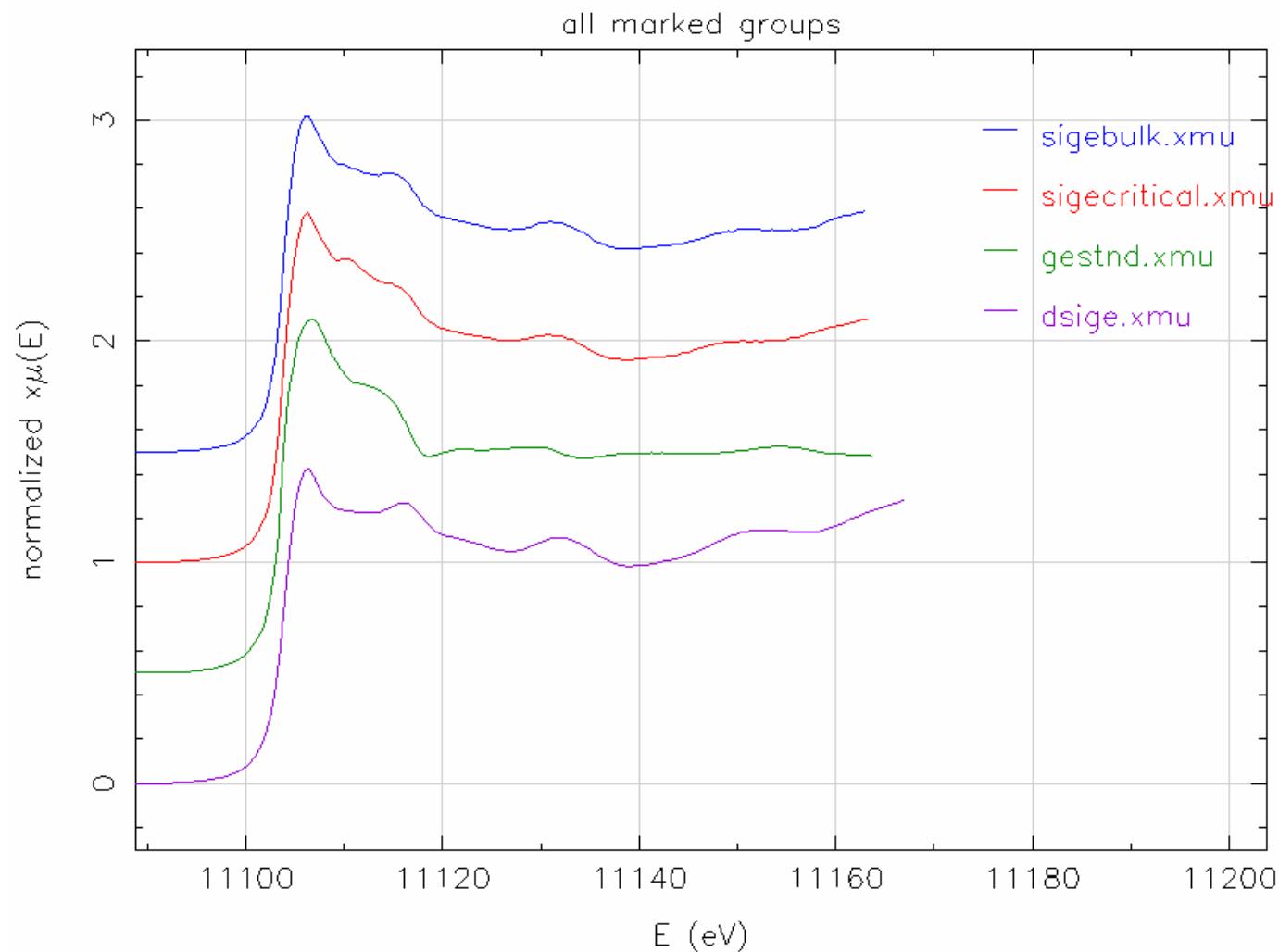
NIST Glancing Incidence XAFS Facility



30 nm SiGe/Si(001)



GIXAFS SiGe/Si(001)

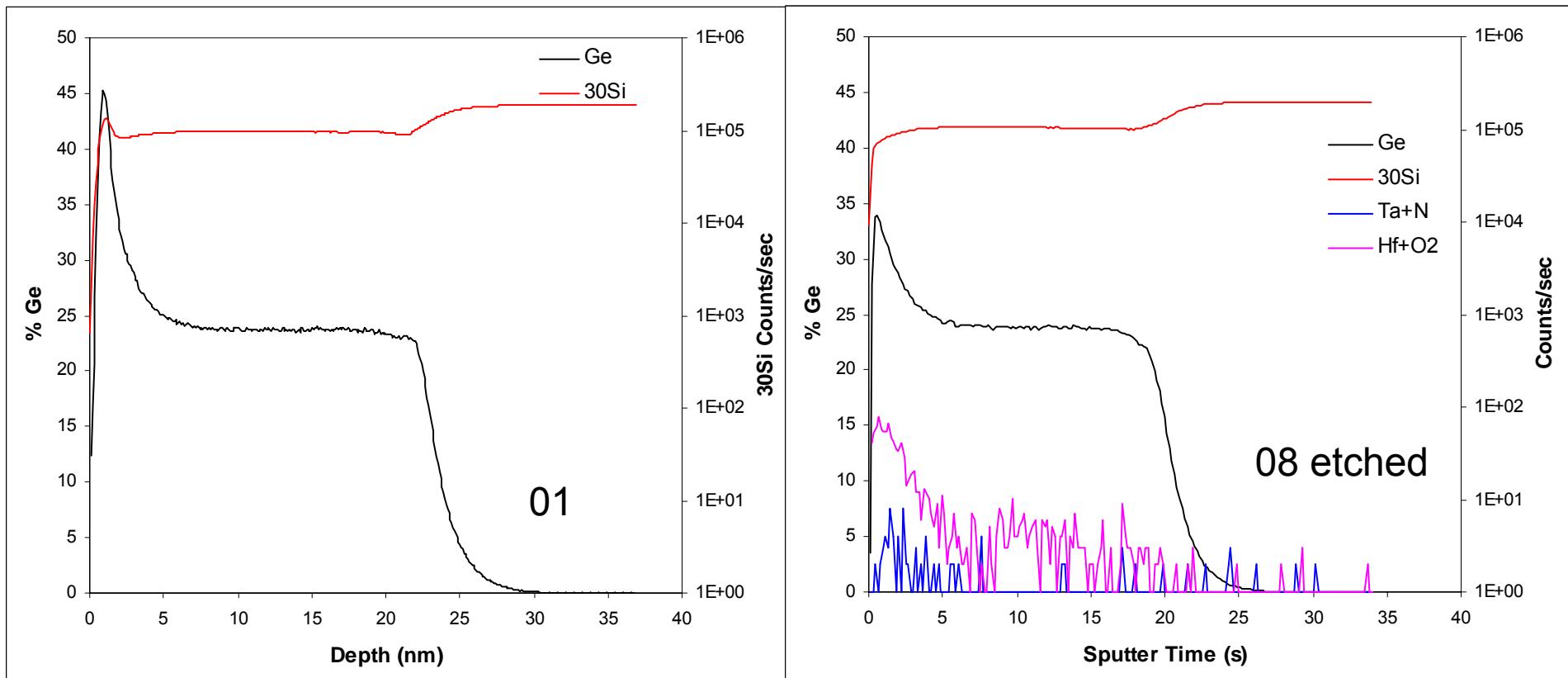


01) Si / 30nm epi SiGe reference piece

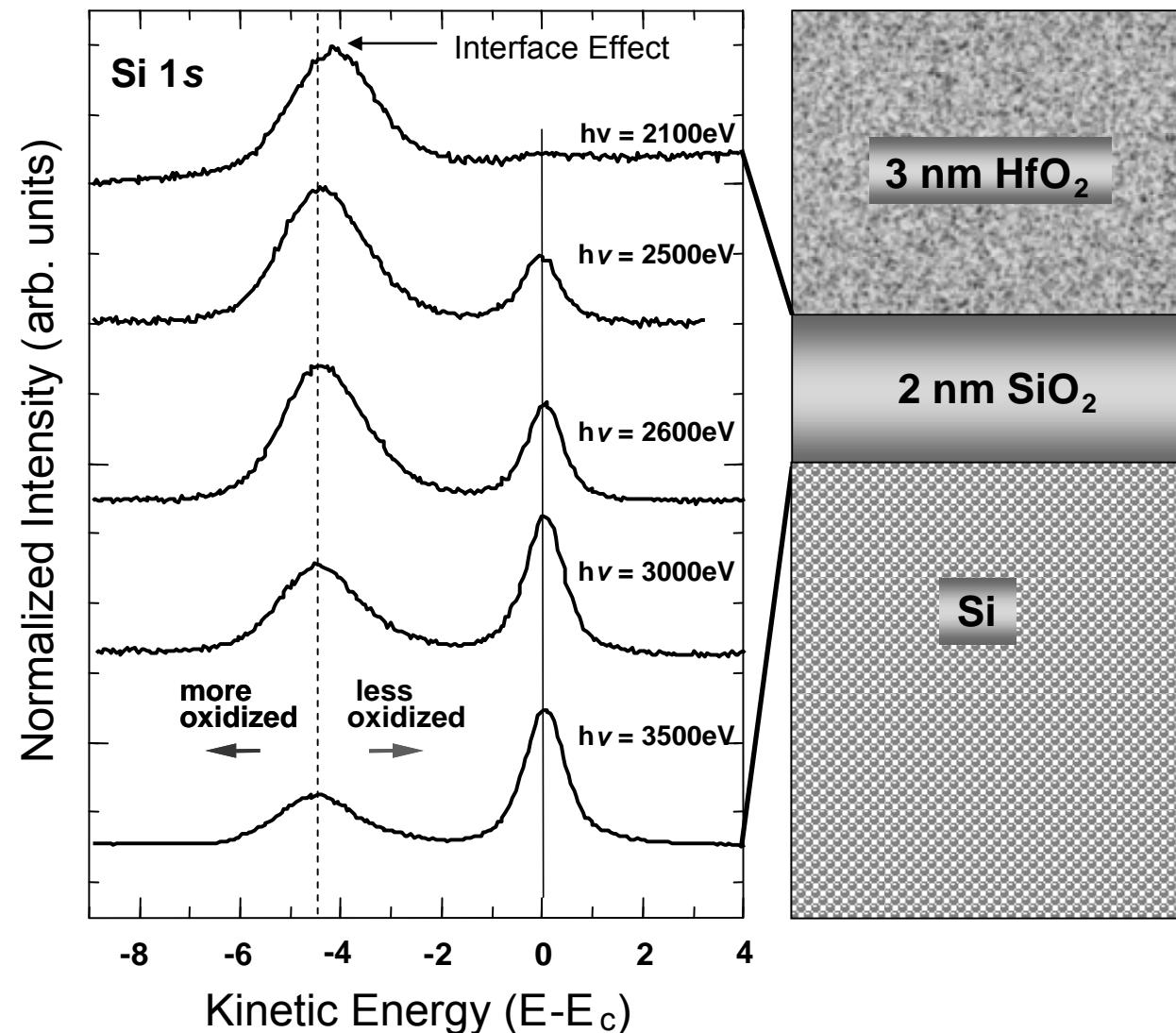
08) Si / 30nm epi SiGe / 2nm HfO₂ / 2.5nm TaN / 950C/N2

- Possible SIMS artifacts:

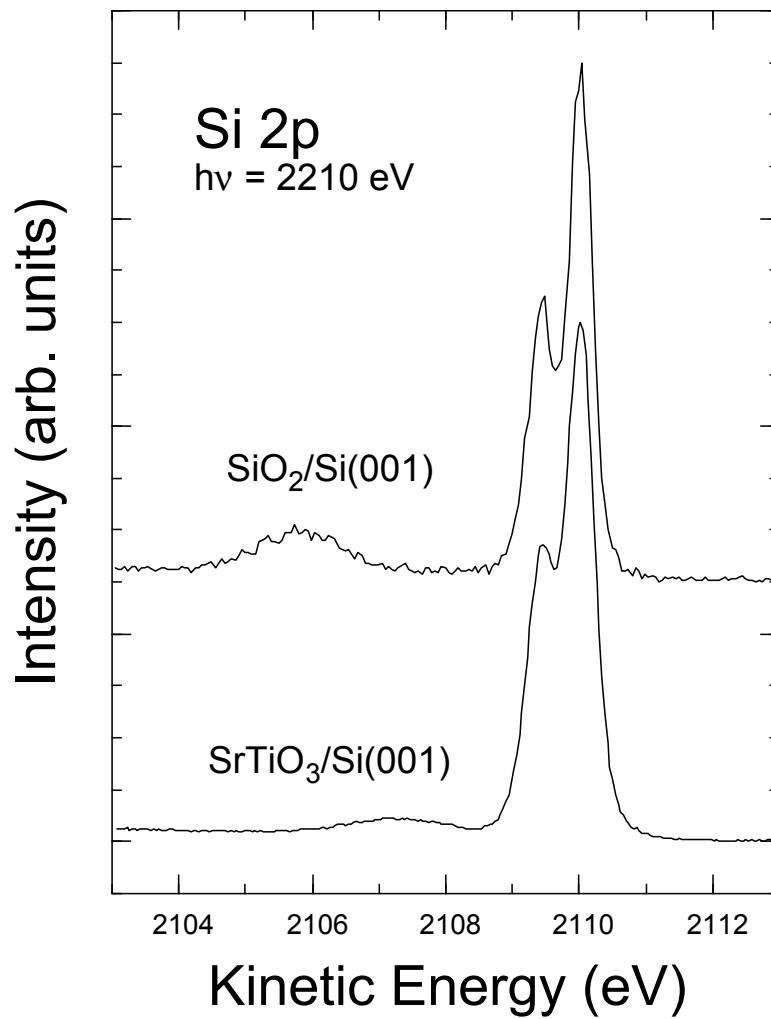
- Sputter rate different at surface vs. bulk.
- Ionization efficiency different at surface vs. bulk.
- Together measurements confirm Ge surface segregation!



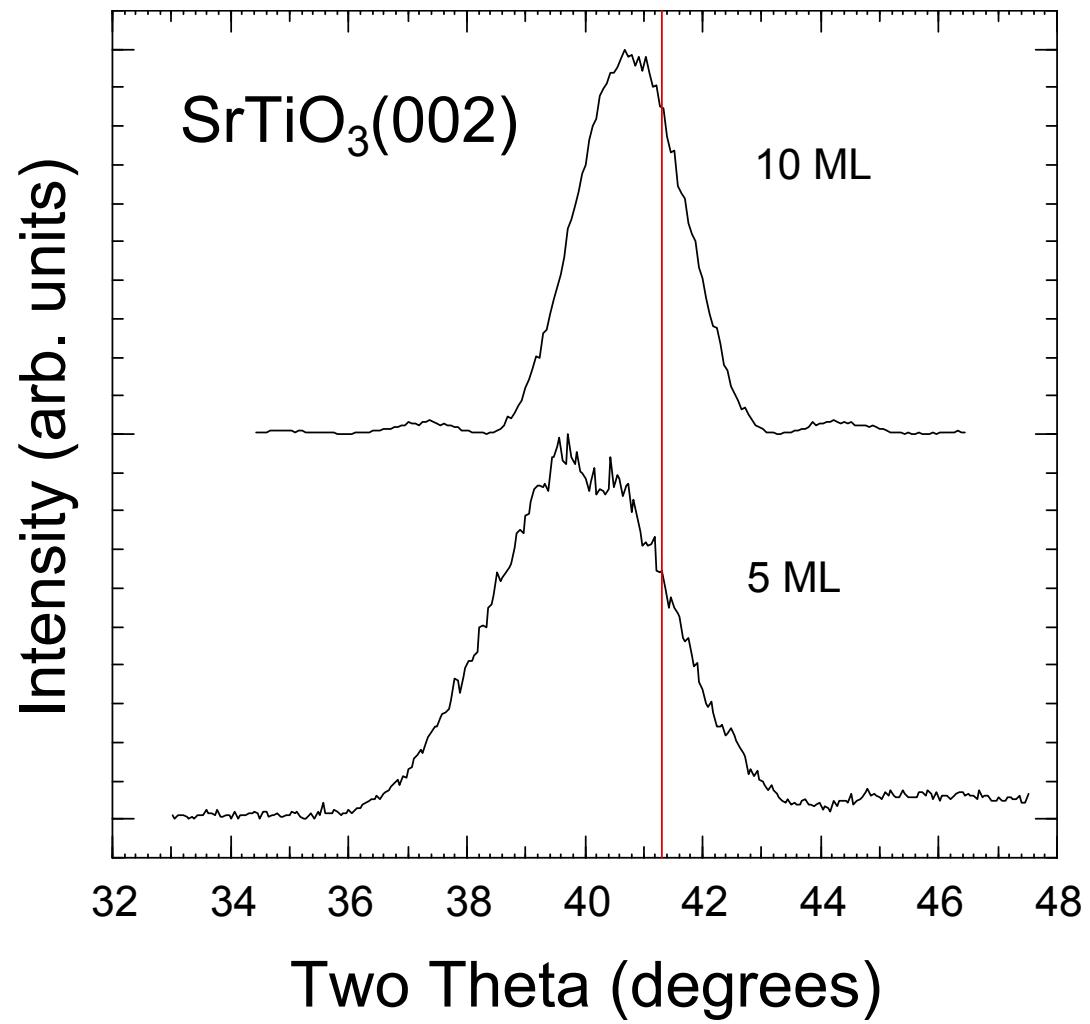
Depth Profiling VKE-HEXPS



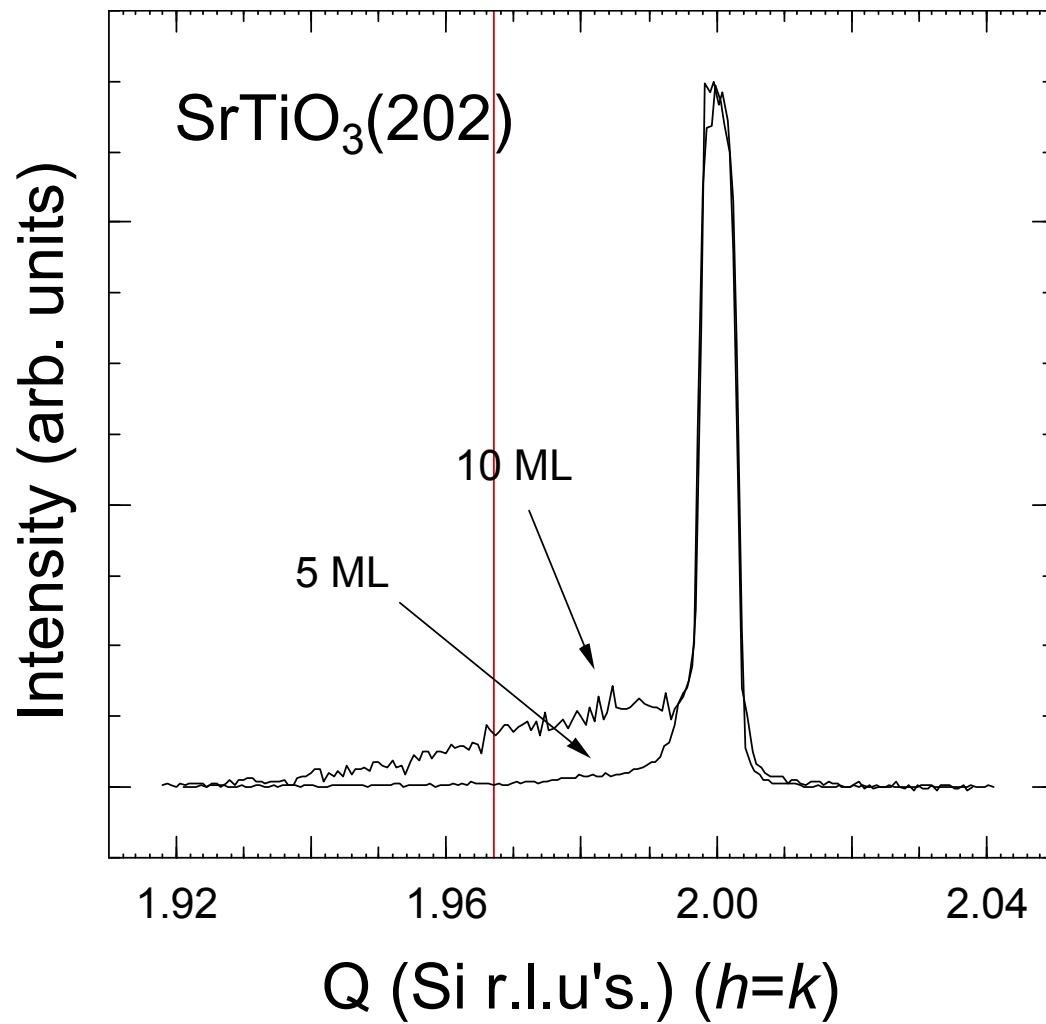
XPS of 5 ML (20 Å) SrTiO_3 films on Si(001)



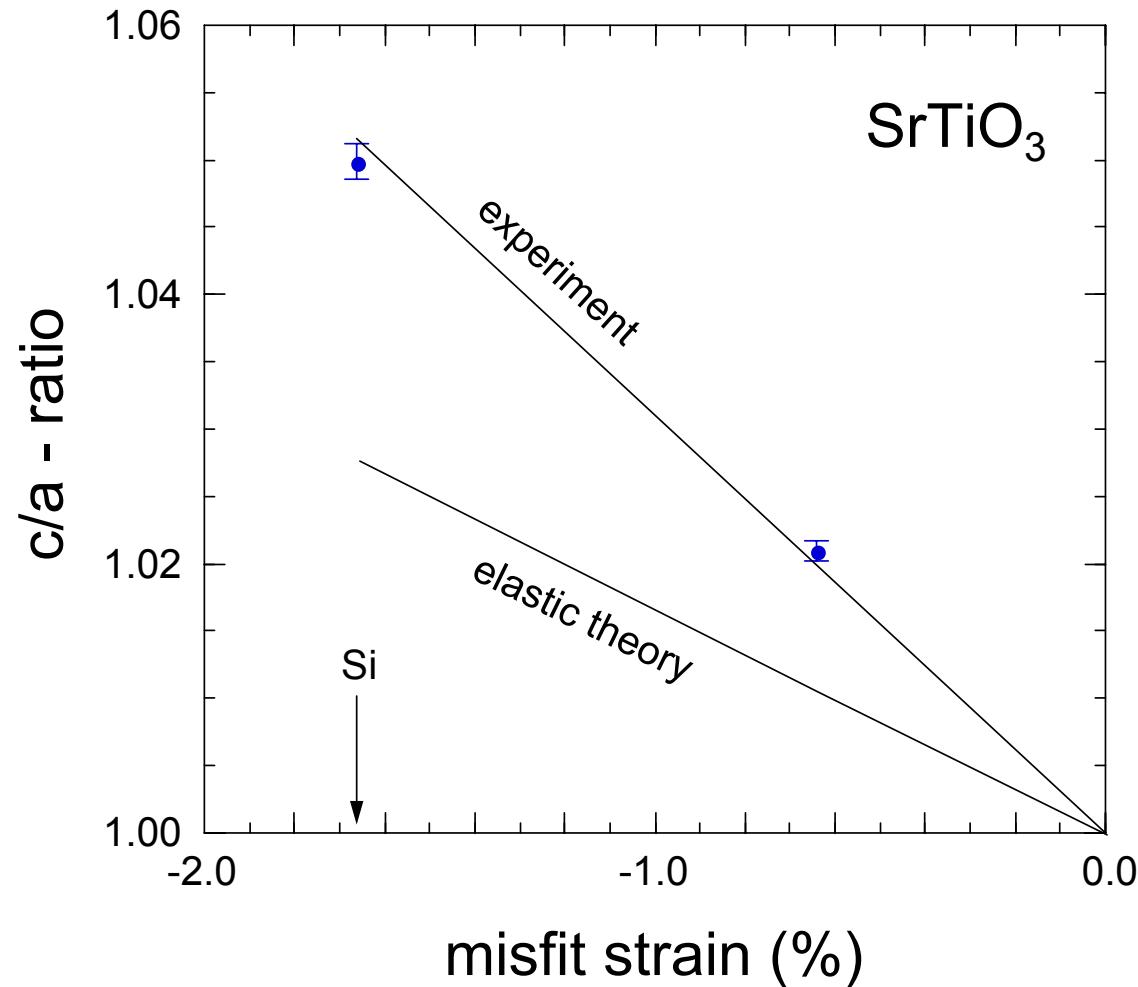
X-ray Diffraction



5 ML films are coherently strained!



Diffraction measurements of SrTiO_3 tetragonal distortion



Crystal Field Splitting – d level chemistry

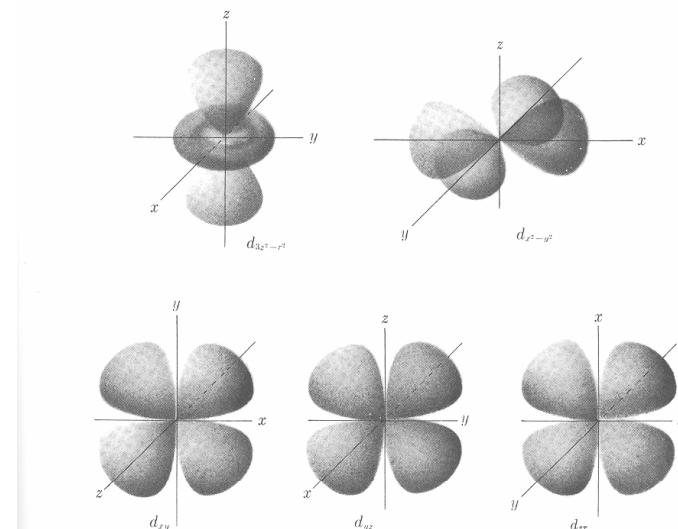


Fig. 5.10. Approximate shapes of d -electron clouds.

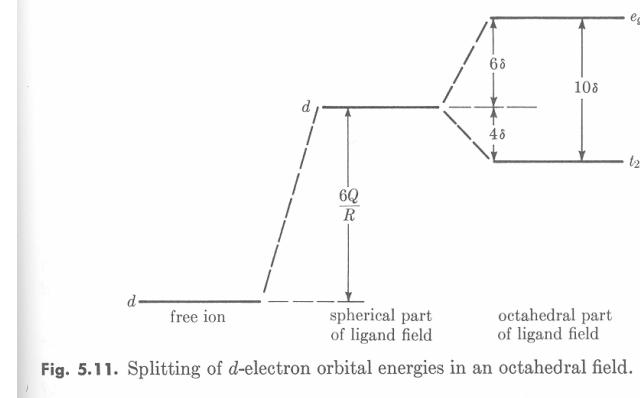


Fig. 5.11. Splitting of d -electron orbital energies in an octahedral field.

Tetragonal Distortion

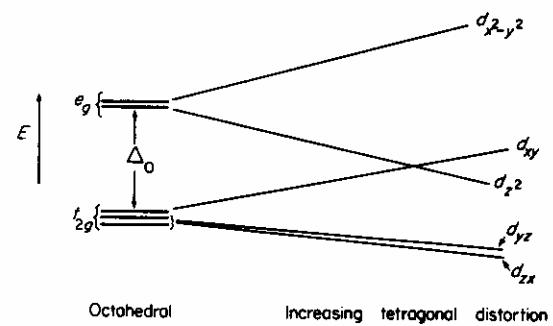
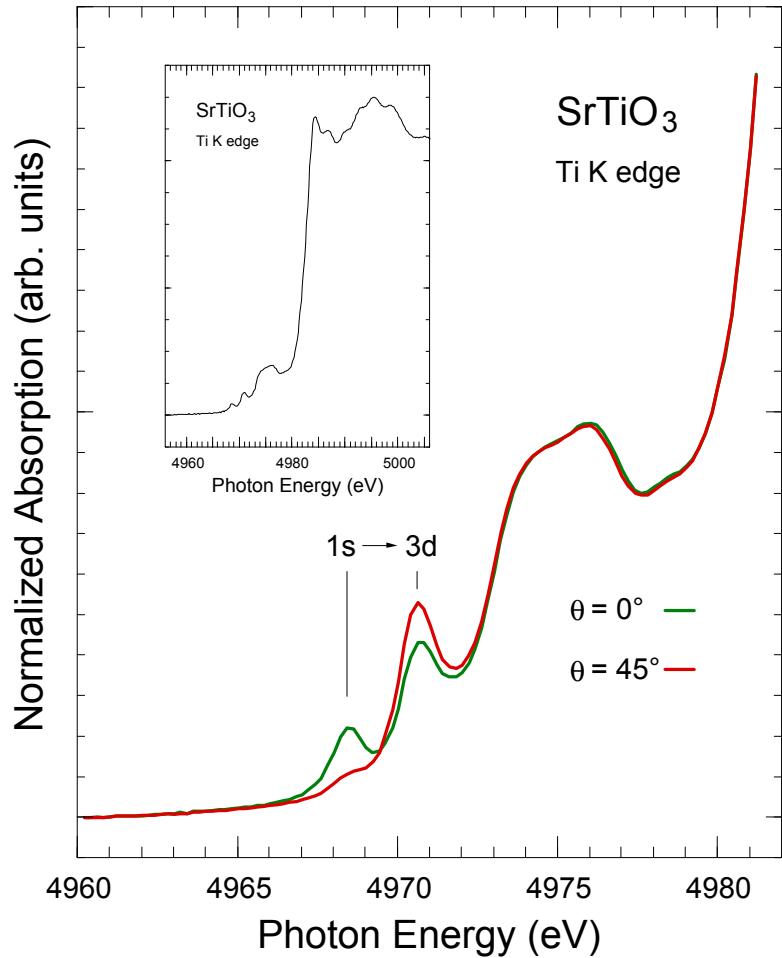
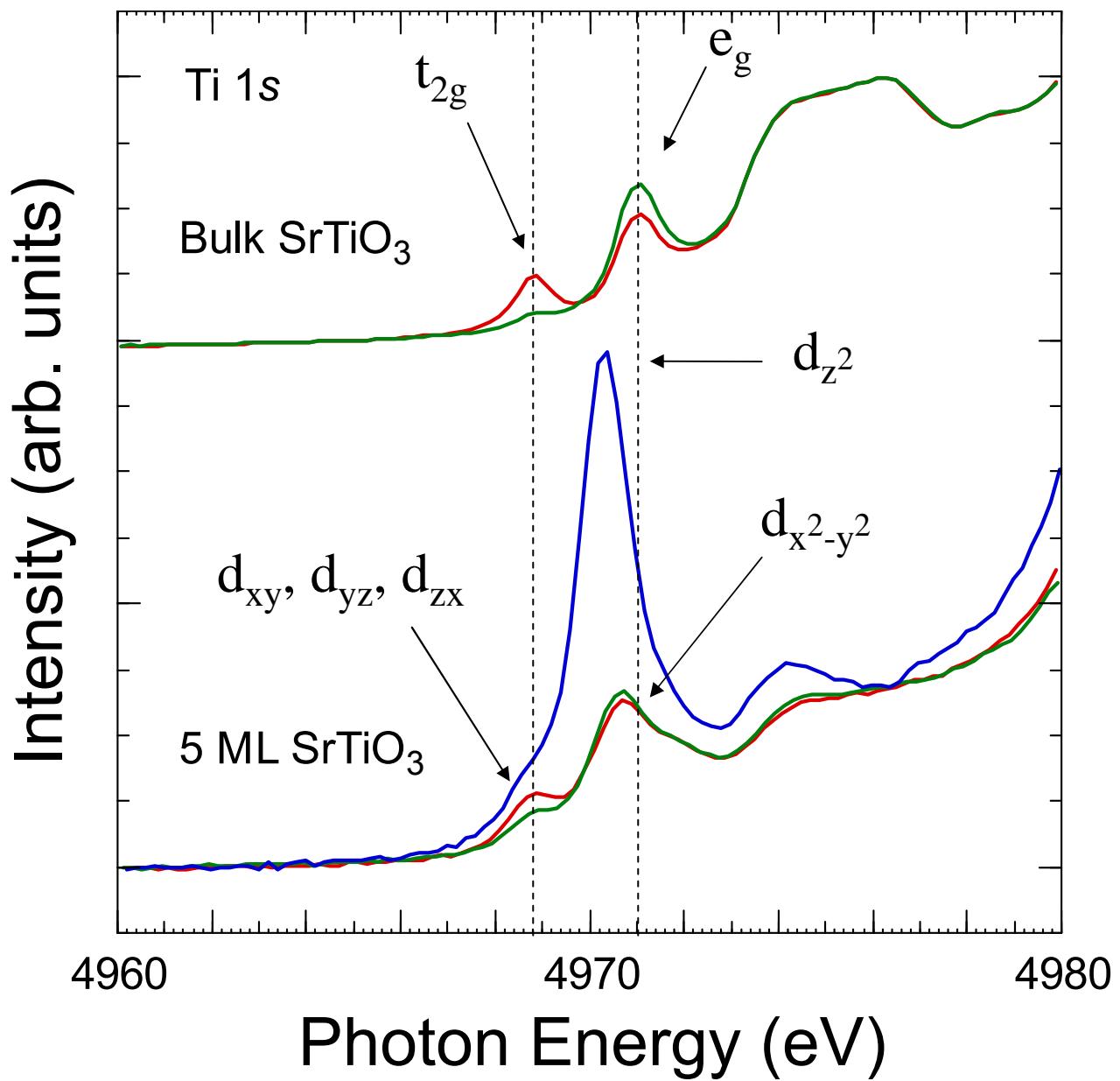


Fig. 20-15. Energy level diagram showing the further splitting of the d orbitals as an octahedral array of ligands becomes progressively distorted by the withdrawal of two *trans* ligands, specifically those lying on the z axis.

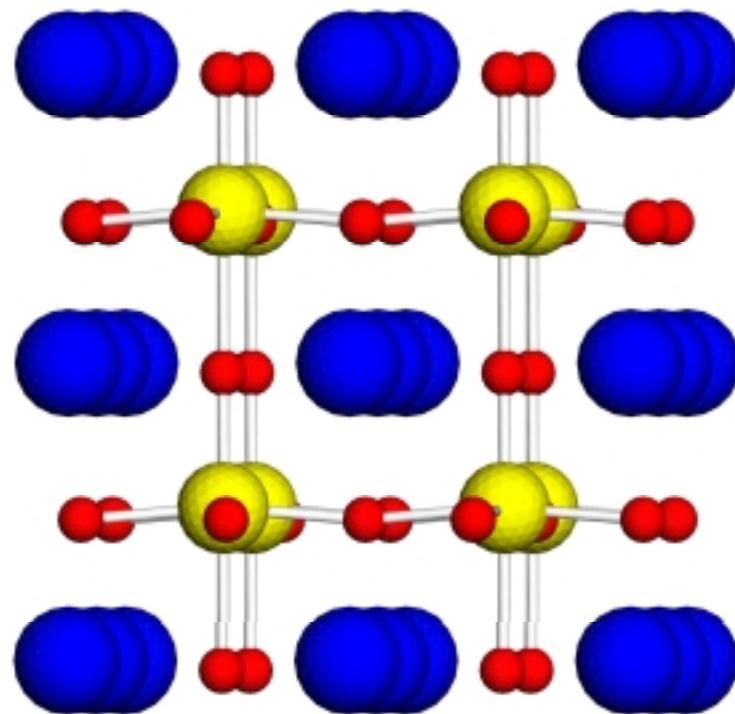
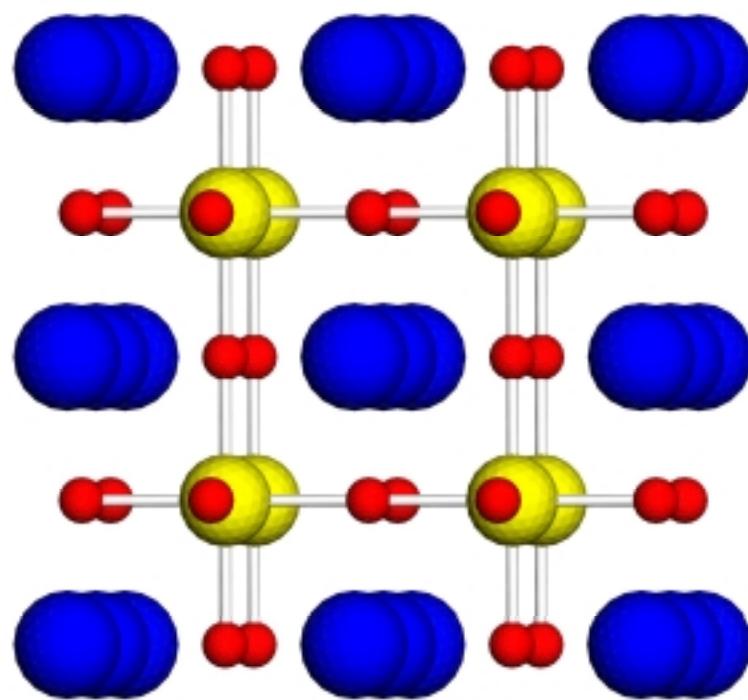
Polarization dependence of Ti K edge of cubic SrTiO₃



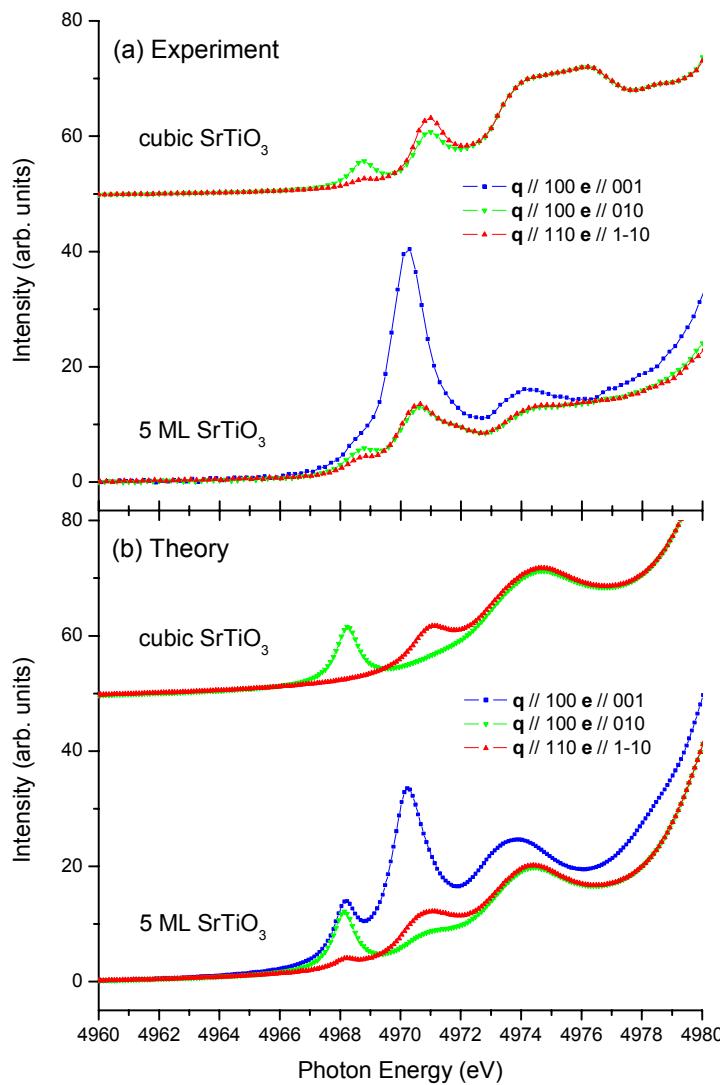
- **Dipole:** $\Delta l = \pm 1$
 $\sigma \propto | \langle f | \epsilon \cdot r | i \rangle |^2$
Ti 1s → 4p
- **Quadrupole:** $\Delta l = \pm 2$
 $\sigma \propto | \langle f | (\epsilon \cdot r)(\mathbf{k} \cdot \mathbf{r}) | i \rangle |^2$
Ti 1s → 3d



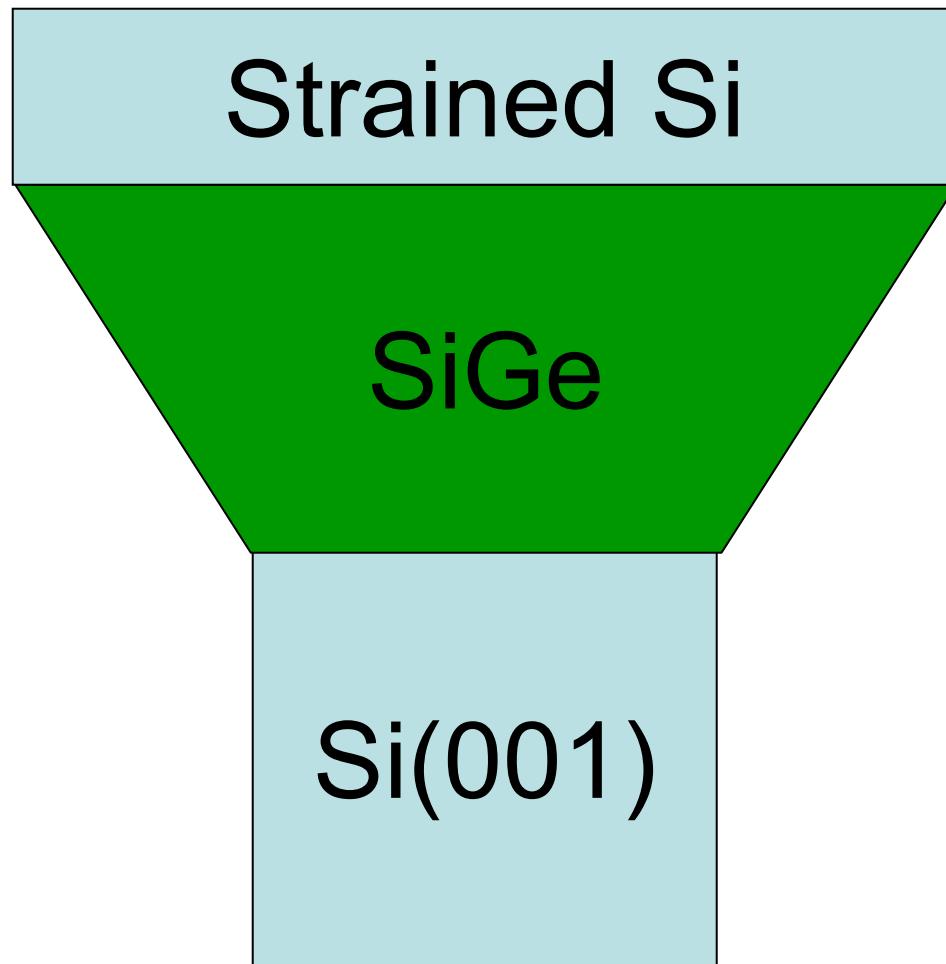
DFT Cubic and Strained SrTiO₃



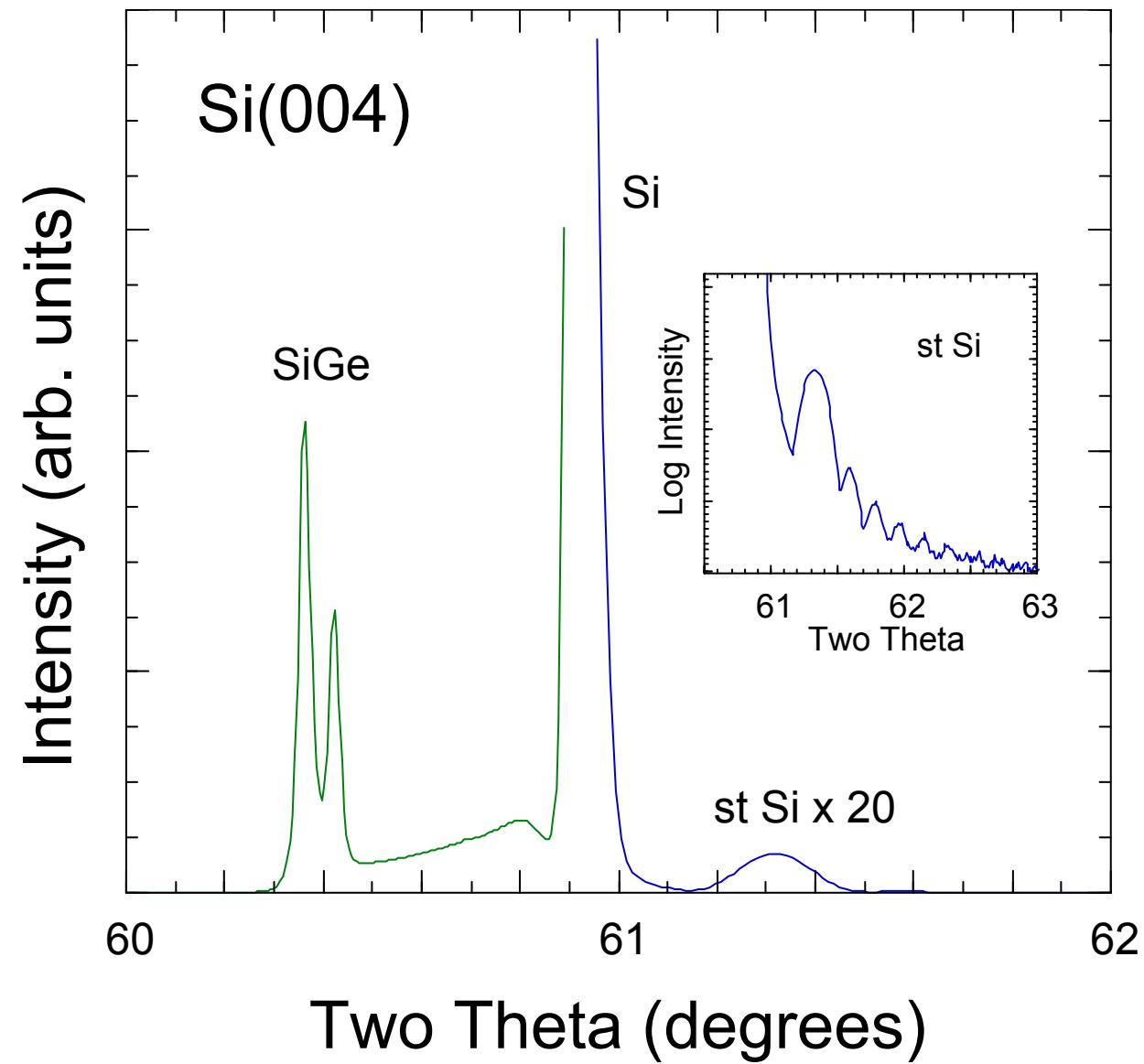
Bethe-Salpeter Calculations of Ti K edge XAFS



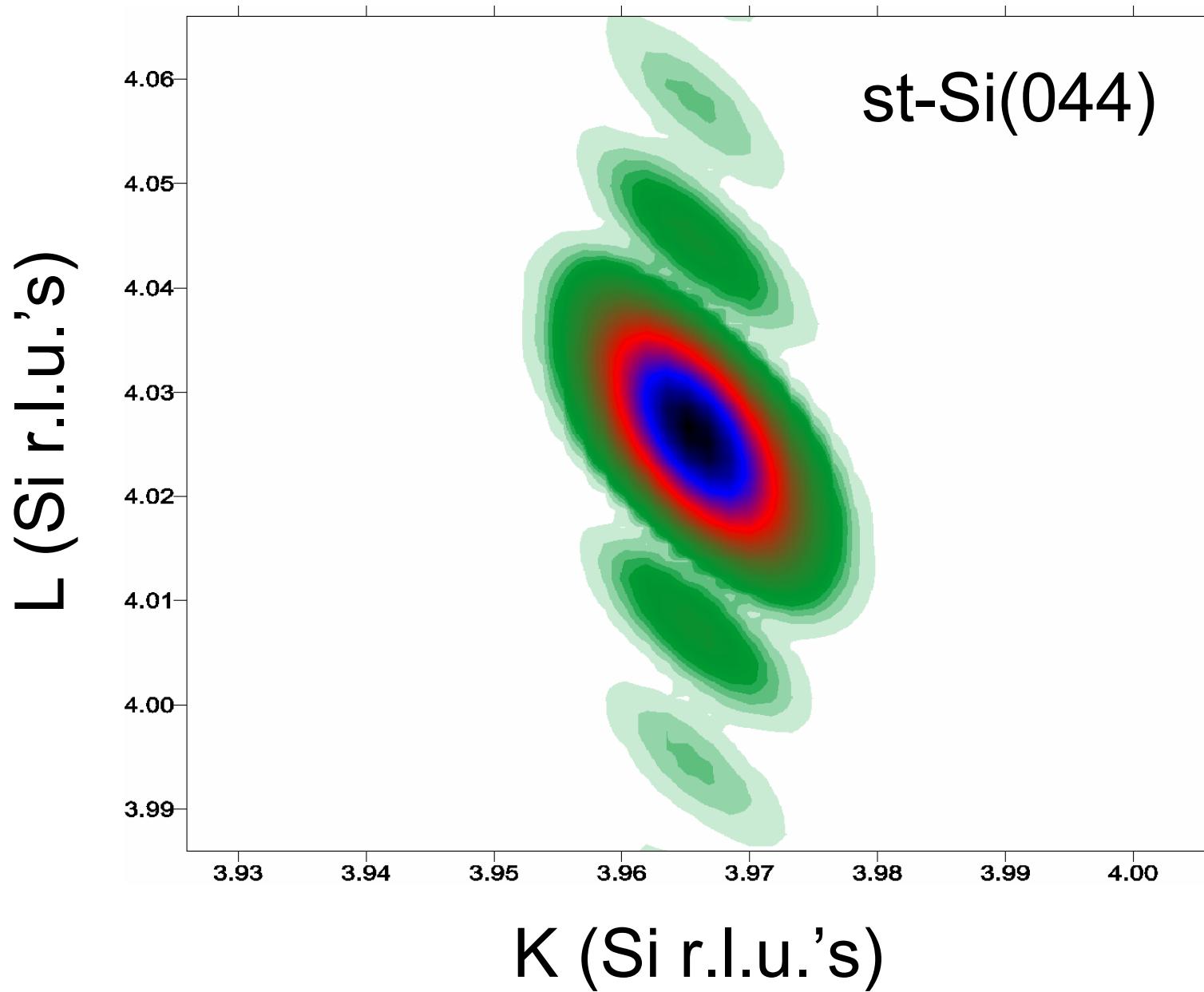
Strained Si on SiGe/Si(001)



X-ray diffraction st-Si/SiGe/Si(001)



Strained-Si on insulator



Conclusions

- *Industry will define the “grand challenges” for NIST.*
- *NIST partners with industry through collaborations and by developing instrumentation for their materials physics needs.*
- *NSLS-II beamlines: XAFS, XRD, NEXAFS, and XPS.*